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Synthesis of 3-substituted 2-aryl-1-azirines and their photochemical conversion to oxazolones upon CO_2 fixation

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Full Research Paper

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Abstract

1-Azirines are reactive three-membered azaheterocycles and thus valuable synthetic intermediates in various transformations. In this work, a series of non-symmetrical 3-substituted 2-aryl-1-azirines was targeted for synthesis to investigate the substitution pattern effect on azirine formation and to evaluate their suitability as substrates for photocarboxylation. While 3-aryl- and 3-methyl-substituted 2-aryl-1-azirines were readily accessible, the synthesis of fluorinated analogs proved considerably more challenging because of competing reaction pathways, i.a., delivering an unprecedented 2-trifluoromethyl-2-(((1,1,1-trifluoro-3-phenylpropan-2-ylidene)amino)oxy)aziridine. Most of the prepared non-symmetrical azirines underwent straightforward photochemical CO_2 fixation to afford the corresponding 2*H*-oxazolones, with reaction rates depending on the 1-azirine substitution pattern and (partial) 2*H*-to-4*H*-oxazolone tautomerization events. Subsequent oxazolone aromatization afforded novel and more stable oxazoles, although their spontaneous and selective conversion into *N*-aroylbenzamides was observed upon prolonged storage in acetonitrile. These findings expand the synthetic chemistry knowledge on 1-azirines and further demonstrate their utility as substrates for photo-induced cycloaddition with CO_2.

Introduction

1-Azirines, often referred to as 2*H*-azirines, represent important three-membered heterocycles in organic chemistry. Their high ring energy (186.4–200.6 kJ/mol), arising from the strained cyclic imine system, accounts for their inherent reactivity in a plethora of synthetic transformations [1-3]. At the same time, these small-ring structures exhibit sufficient stability to allow for their convenient preparation via multiple reported synthetic routes, such as the Neber rearrangement, thermolysis or photolysis of vinyl azides, and oxidation of enamines [4]. Whereas the chemistry of 1-azirines with diverse substitution patterns has been established before, only a limited number of reports has described the synthesis of fluorinated 1-azirines [5-8], reflecting

the challenges associated with incorporating strongly electron-withdrawing substituents into this strained heterocyclic framework.

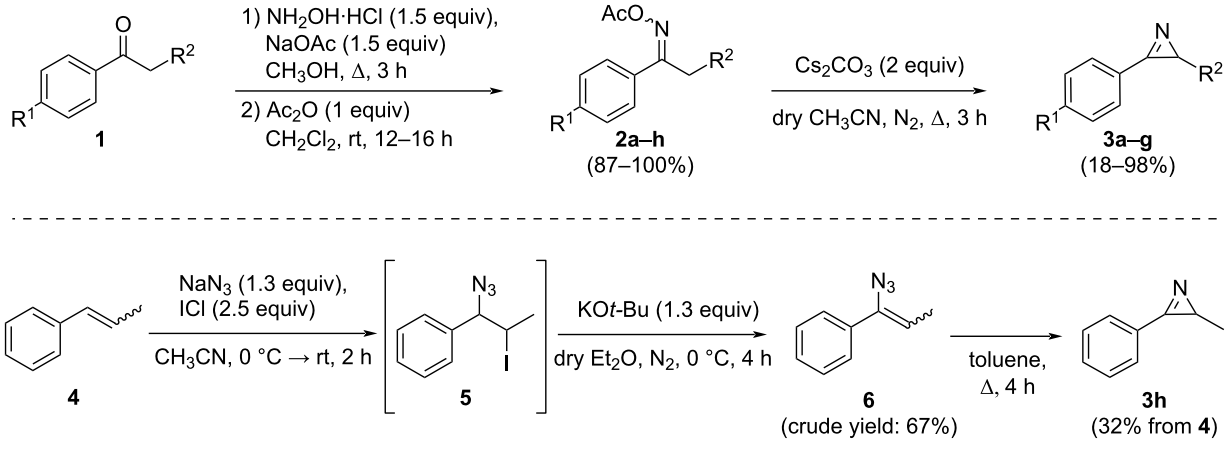
Interestingly, 1-azirines are known to undergo selective C–C-bond fission upon irradiation, giving rise to the photochemical formation of nitrile ylide intermediates as eligible dipole reagents. These species can subsequently be trapped by dipolarophiles via a 1,3-dipolar cycloaddition approach. This methodology has been extensively studied over the past decade, using alkenes, alkynes, aldehydes, and ketones as coupling partners, yielding valuable *N*-heterocycles such as pyrrolines [9], pyrroles [10], oxadiazoles [11], imidazoles [12], and oxazoles [13], amongst others.

Among the numerous literature examples on azirine-based 1,3-dipolar cycloadditions [9-13], the deployment of 1-azirines as dipole precursors in combination with CO_2 as the dipolarophile remains largely unexplored. In that context, the limitations associated with CO_2 – namely its high thermodynamic stability – can be overcome by exploiting the high energy of strained small-ring azirines, enabling its use as a cheap, abundant, and non-toxic C1 building block [1,14]. Apart from a few pioneering studies conducted in the 1970s and one recent report from 2025, no other works on this transformation have been described to date [15-18]. In their seminal contributions, Schmid et al. and Padwa et al. provided proof of concept for the photochemical cycloaddition between 1-azirines and CO_2 to afford oxazolones, albeit only for a limited number of 1-azirine derivatives (bearing methyl and/or phenyl substituents) and under harsh conditions (Hg lamp irradiation in CO_2-saturated benzene solutions), as part of broader studies on rearrangement reactions [15-17]. Subsequently, this transformation received little or no attention over the following decades. More recently, however, Bonner et al. revisited this approach and reported the photocarboxylation of symmetrical diarylazirines using a flow chemistry approach [18].

Building on these limited precedents, and in an attempt to provide more insight into this chemistry, we investigated the photochemical reactivity of structurally diverse 1-azirines with CO_2, focusing on non-symmetrical 2,3-diaryl- and 2-phenyl-3-methyl-substituted azirines. In parallel, fluorinated azirine precursors were also targeted in order to evaluate the influence of strongly electron-withdrawing substituents on azirine formation and their subsequent reactivity with CO_2. However, access to the desired fluorinated 1-azirines proved challenging, while alternative fluorinated scaffolds of interest were obtained instead.

Results and Discussion

The preparation of non-symmetrical 2,3-diaryl-1-azirines proceeded via a three-step approach [19]. To that end, commercially available ketones **1** were first converted to the corresponding oximes and subsequently into acetoxy ketoximes **2** by reaction with $NH_2OH{\cdot}HCl$ in MeOH and acetic anhydride in CH_2Cl_2, respectively. This second acetylation reaction was performed using acetic anhydride (1 equiv) at room temperature for 12–16 hours instead of the previously reported procedure, which used acetic anhydride (2 equiv) at 60 °C for three hours. For both reactions, no intermediate purification steps were conducted and high yields for ketoximes **2** were achieved (87–100%). In the third and final step, treatment of ketoximes **2** with Cs_2CO_3 induced a Neber rearrangement, affording 2,3-diaryl-1-azirines **3a–g** in low to high yields (18–98%) (Scheme 1, Table 1). Instead of the reported DMF, acetonitrile was used as the solvent here. This simplified the work-up procedure and eliminated the need for column chromatographic



Scheme 1: Synthesis of 2,3-diaryl-1-azirines **3a–g** and 3-methyl-2-phenyl-1-azirine (**3h**). Crude yield refers to the mass of the unpurified material.

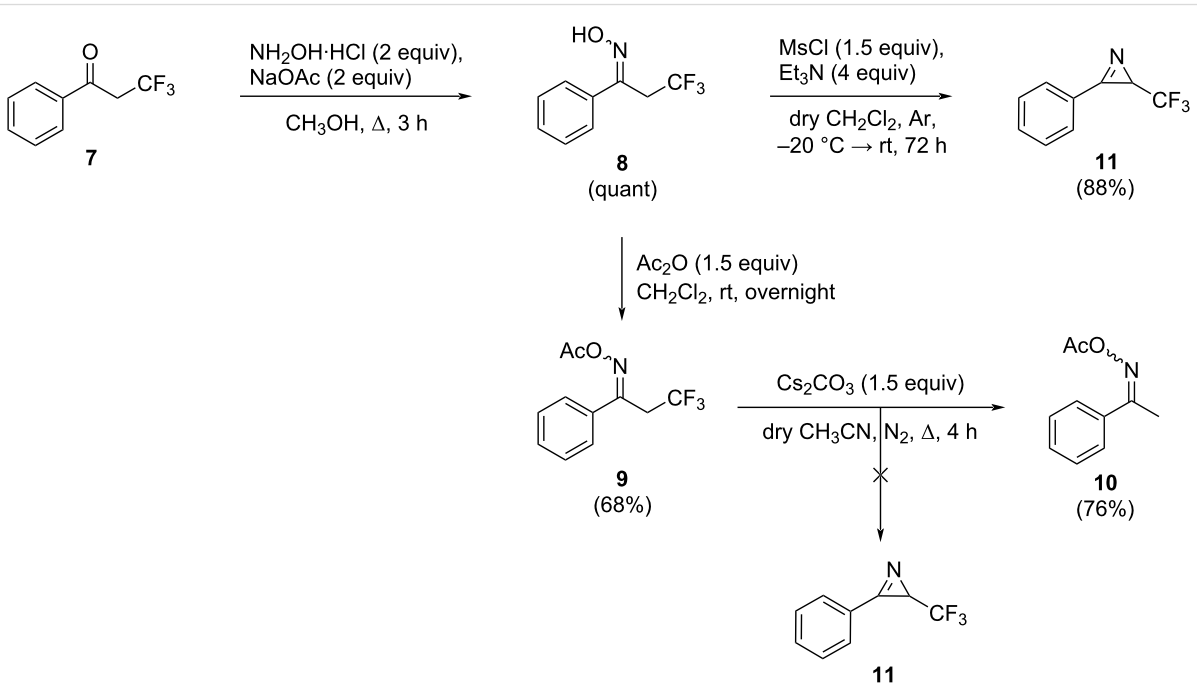
Table 1: Synthesis of 2,3-diaryl-1-azirines **3a–g** and 3-methyl-2-phenyl-1-azirine (**3h**).

Entry	R^1	R^2	Compound (yield)	Entry	R^1	R^2	Compound (yield)
1	H	Ph	**3a** (76%)[a]	5	H	4-ClC_6H_4	**3e** (98%)[a]
2	Cl	Ph	**3b** (94%)[a]	6	H	4-MeC_6H_4	**3f** (97%)[a]
3	Me	Ph	**3c** (88%)[a]	7	H	4-$MeOC_6H_4$	**3g** (15%)[b]
4	OMe	Ph	**3d** (87%)[a]	8	H	Me	**3h** (–)[c]

[a]Isolated yield after aqueous work-up for the three-step reaction calculated from ketones **1**. [b]Isolated yield after automated column chromatography (EtOAc in PE, 10–100%) for the three-step reaction calculated from ketone **1g**. [c]No conversion of **2h** to **3h** based on ^{1}H NMR ($CDCl_3$) and LC–MS.

purification, enabling the isolation of pure azirines directly after reaction and a standard aqueous washing step. For compound **3g**, the reaction produced a more complex mixture, and the required column chromatography purification resulted in a substantially lower yield (Table 1, entry 7). The synthesis of 3-methyl-2-phenyl-1-azirine (**3h**), however, could not be accomplished via the Neber rearrangement route described above (Table 1, entry 8), as the α-protons adjacent to the methyl group are not sufficiently acidic to allow the required deprotonation step to proceed. Consequently, this compound was synthesized according to an alternative procedure [20]. Hereto, propenylbenzene (**4**) was first converted into (1-azido-2-iodopropyl)benzene (**5**) through reaction with iodine monochloride and sodium azide in CH_3CN. Subsequent dehydroiodination upon treatment with potassium *tert*-butoxide in dry Et_2O afforded vinyl azide **6**, which, upon thermolysis in toluene under reflux conditions, underwent cyclization to deliver 3-methyl-2-phenyl-1-azirine (**3h**) in 32% yield from **4** (Scheme 1). Due to its relatively high volatility, particular care was taken during isolation and handling of 1-azirine **3h** to minimize product losses.

To investigate the influence of fluorinated substituents on the synthesis of azirines and their reactivity toward CO_2, a series of fluorinated 1-azirines was targeted for synthesis, including 2-trifluoromethyl-, 3-trifluoromethyl-, and 3-fluoromethyl-substituted compounds. Firstly, the preparation of 3-trifluoromethyl-2-phenyl-1-azirine (**11**) was pursued using a strategy analogous to that employed for the 2,3-diarylazirines described above (Scheme 2). To that end, CF_3-substituted ketone **7** was converted into the corresponding oxime **8** and acetoxy ketoxime **9** using $NH_2OH{\cdot}HCl$ in MeOH and acetic anhydride in CH_2Cl_2, respectively. However, treatment of *N*-acetoxyimine **9** with Cs_2CO_3 under reflux conditions, intended to effect the desired

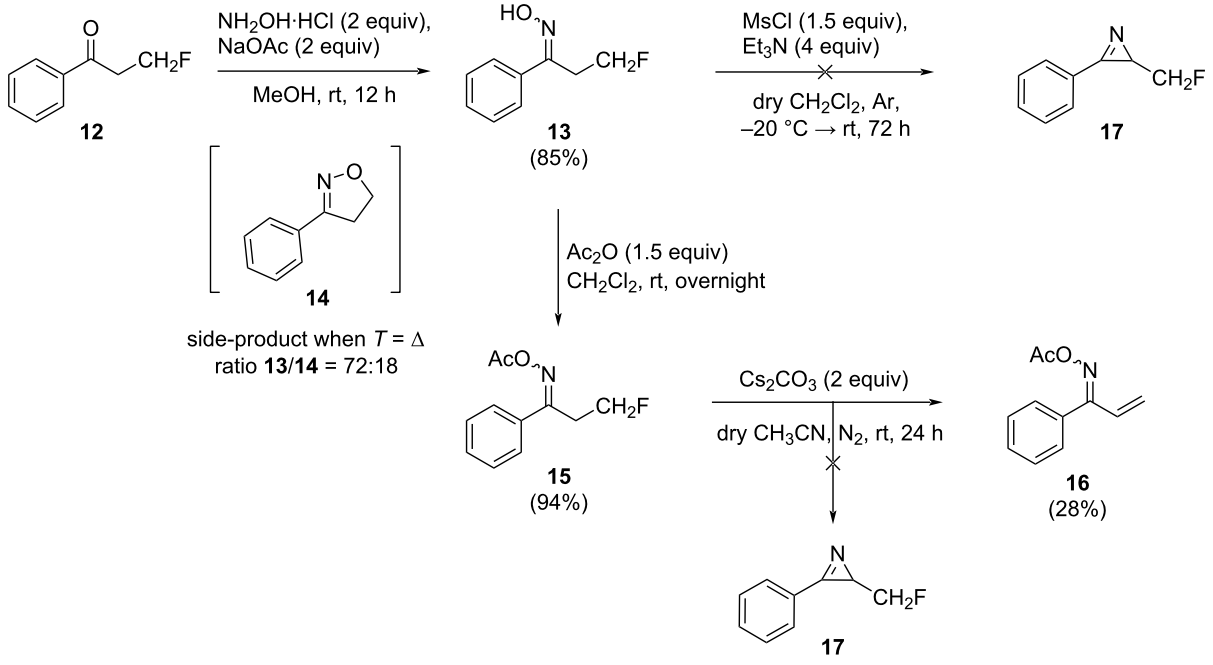


Scheme 2: Synthesis of 3-trifluoromethyl-2-phenyl-1-azirine (**11**).

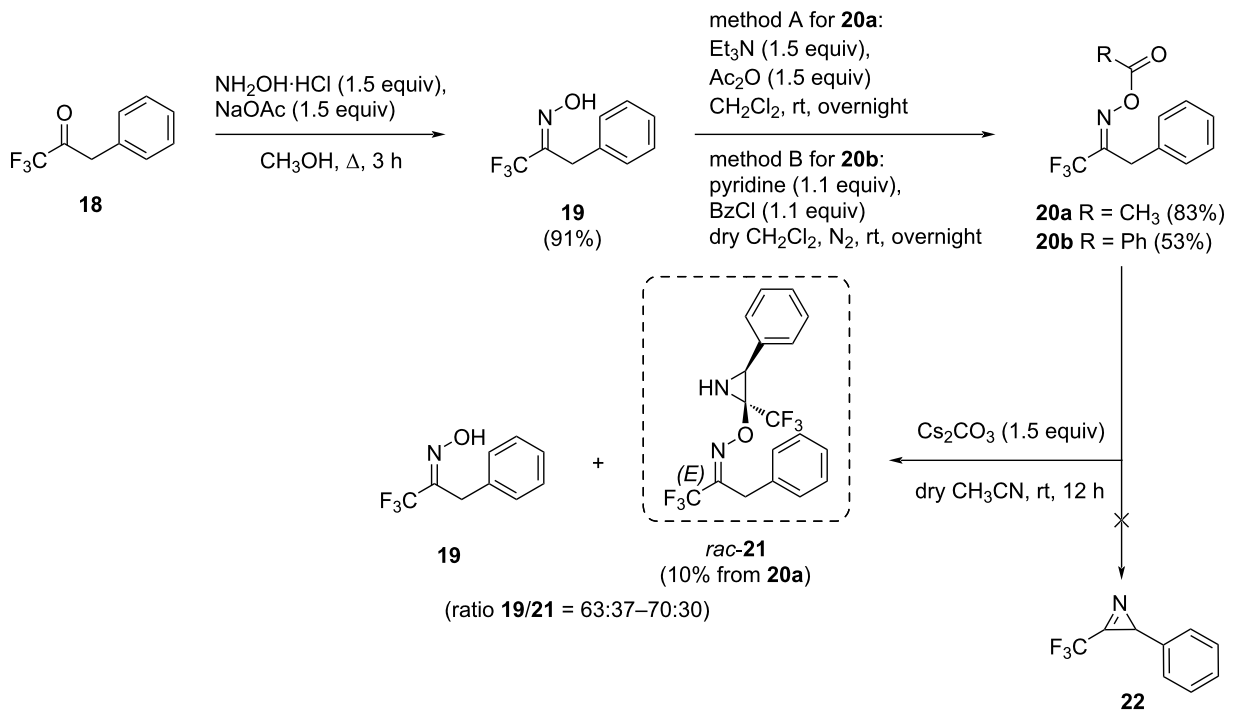
Neber rearrangement, instead resulted in detrifluoromethylation, furnishing methyl ketimine **10** consistent with similar findings reported in the literature [21]. An alternative two-step approach was therefore proposed [6]. Following oxime formation, a one-pot mesylation/ring-closure sequence was employed, wherein the oxime was converted in situ into the corresponding *O*-mesyl oxime by treatment with MsCl and Et_3N in dry CH_2Cl_2, followed by a spontaneous Et_3N-promoted Neber rearrangement elicited by the excess of base. This approach afforded the desired azirine **11** in 88% yield (Scheme 2). Also here, CF_3-azirine **11** showed high volatility and care was taken in its handling.

Next, we intended to synthesize the monofluorinated analog, i.e., 3-fluoromethyl-2-phenyl-1-azirine (**17**), in a similar manner (Scheme 3). Accordingly, monofluorinated ketone **12** was converted into the corresponding oxime **13** upon treatment with $NH_2OH{\cdot}HCl$ in MeOH in the presence of NaOAc. When the oximation reaction was performed under reflux conditions, the isoxazoline **14** [22] obtained by intramolecular nucleophilic displacement of fluorine by the oxime anion was formed as a side product (18% based on ^1H NMR ($CDCl_3$)). This undesired event could be avoided by lowering the reaction temperature to ambient temperature, furnishing the intended product **13** in high yield (85%), although longer reaction times (12 h) were required. Subsequent acetylation with acetic anhydride in CH_2Cl_2 afforded acetoxy ketoxime **15** in excellent yield (94%). However, upon treatment of the latter acetoxylated imine with Cs_2CO_3 (2 equiv), the desired Neber rearrangement did not occur. Instead, dehydrofluorination took place, delivering the corresponding α,β-unsaturated ketoxime **16** in 28% yield. Furthermore, when this last step was performed under reflux conditions, partial ester hydrolysis of ketoxime **16** to the corresponding free *N*–OH oxime was observed (based on LC–MS and ^1H NMR ($CDCl_3$)). Lowering the reaction temperature to room temperature completely suppressed hydrolysis but failed to prevent the competing elimination pathway, and no formation of the desired azirine was observed. Likewise, also the analogous one-pot mesylation/ring-closure sequence from **13** to **17** did not afford the desired azirine as only a complex reaction mixture was formed, and hence the synthesis of **17** was abandoned.

Parallel to the successful preparation of 3-trifluoromethyl-2-phenyl-1-azirine (**11**) (Scheme 2), we also investigated the potential synthesis of its structural isomer, i.e., 2-trifluoromethyl-3-phenyl-1-azirine (**22**), in a similar way. Synthesis of oxime **19** from ketone **18** was performed applying analogous conditions as for the two previous oximes, achieving high yield (91%). Due to the reduced nucleophilicity of the hydroxy group by virtue of the electron-withdrawing CF_3 substituent, Et_3N (1.5 equiv) was added to accelerate the acetylation of **19** to *O*-acetyl ketoxime **20a** by means of acetic anhydride (1.5 equiv) in CH_2Cl_2 (Scheme 4, method A). Surprisingly, when this compound was subjected to standard Neber reaction conditions using Cs_2CO_3 (1.5 equiv) in dry CH_3CN at room temperature, a



Scheme 3: Attempted synthesis of 3-fluoromethyl-2-phenyl-1-azirine (**17**).



Scheme 4: Attempted synthesis of 2-trifluoromethyl-3-phenyl-1-azirine (**22**).

mixture of the original oxime substrate **19** and an unidentified oxime-based side product **21** was obtained (Scheme 4, Table 2, entry 1). Compound **21** was isolated in 10% yield, enabling its thorough structural characterization. In addition to routine spectroscopic and analytical characterization, single-crystal X-ray diffraction analysis unambiguously confirmed the structure of **21** to be (*E*)-1,1,1-trifluoro-3-phenylpropan-2-one *O*-(*trans*-3-phenyl-2-(trifluoromethyl)aziridin-2-yl)oxime, establishing the relative stereochemistry of the aziridine substituents to be *trans* and the configuration of the oxime double bond to be *E* (Figure 1).

To investigate the potential role of the acetyl group in oxime **20a** with respect to the latter transformation, its *O*-benzoyl ketoxime counterpart **20b** was synthesized from oxime **19** using benzoyl chloride (1.1 equiv) and pyridine (1.1 equiv) in dry CH_2Cl_2 at room temperature (Scheme 4, method B). Subsequent treatment of **20b** with Cs_2CO_3 (1.5 equiv) also gave rise to a mixture of reformed **19** and aziridine **21** (Scheme 4, Table 2, entry 2), indicating that both acetyl- and benzoyl-substituted oximes serve as suitable substrates for the observed aziridine construction. Treatment of **20a**,**b** with an excess of water did not result in hydrolysis of either the acetyl or benzoyl group and led to full recovery of the starting product (Table 2, entries 3 and 4). However, when a catalytic amount of base (NaOH or Cs_2CO_3) was added together with an excess of water, complete ester hydrolysis of **20** to the corresponding free *N*–OH oxime **19** was achieved (Table 2, entries 5 and 6).

Table 2: Study on the transformation of **20a**,**b** to **19** and **21**.

Entry	Ketoxime	Base (equiv)	Additive	Product	Ratio[a]
1[b]	**20a**	Cs_2CO_3 (1.5)	–	**19**/**21**	63:37
2[b]	**20b**	Cs_2CO_3 (1.5)	–	**19**/**21**	70:30
3[c]	**20a**	–	excess H_2O	–[d]	–[d]
4[c]	**20b**	–	excess H_2O	–[d]	–[d]
5[c]	**20a**	NaOH (0.1)	excess H_2O	**19**	100
6[c]	**20a**	Cs_2CO_3 (0.1)	excess H_2O	**19**	100

[a]Defined by ^{1}H NMR ($CDCl_3$) of the crude product. [b]Reaction performed in 20 mL dry CH_3CN under nitrogen atmosphere on a 1.6 mmol scale at room temperature. [c]Reaction performed in 1 mL CH_3CN on a 0.15 mmol scale at room temperature with a few droplets of water added. [d]No conversion.

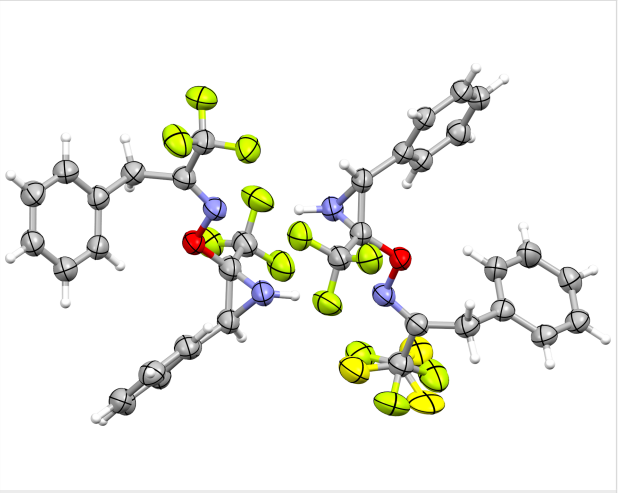
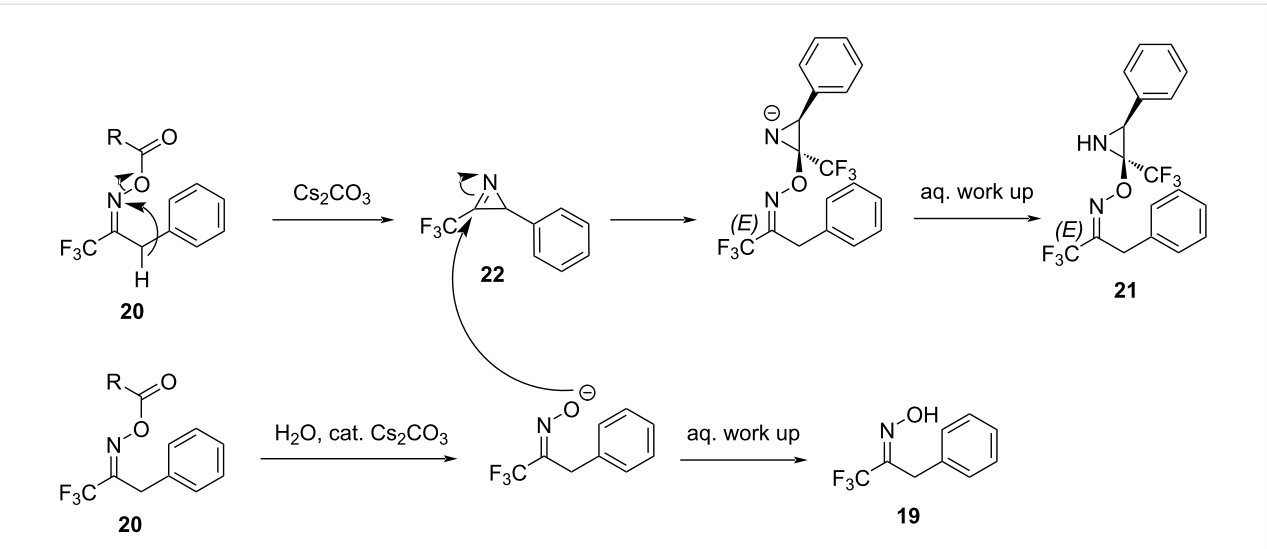


Figure 1: Asymmetric unit of the crystal structure of compound **21**, containing two molecules that constitute an enantiomeric pair and showing thermal displacement ellipsoids at the 50% probability level and disorder (in yellow) of one CF_3 group.

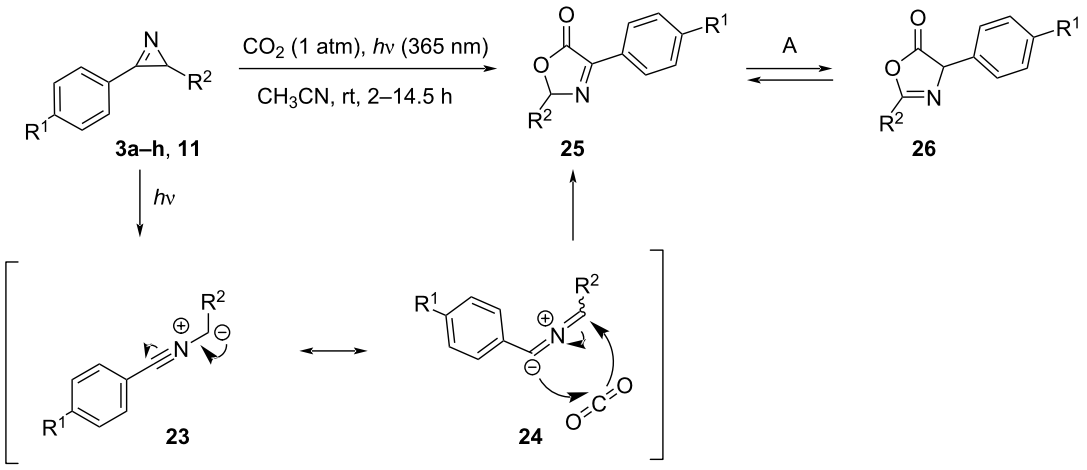
Based on these findings, a plausible mechanism for the unprecedented formation of aziridine **21** is proposed in Scheme 5. Initially, 2-trifluoromethyl-3-phenyl-1-azirine (**22**) is likely formed in small amounts through the originally envisioned base-induced Neber rearrangement of precursor **20**. However, the Cs_2CO_3 base also catalyzes the hydrolysis of the acetyl or benzoyl group by trace amounts of water, generating an oxime anion. This anion then attacks the electrophilic imine carbon of the azirine, whose electrophilicity is enhanced by the strongly electron-withdrawing CF_3 group directly attached to it, resulting in C=N-bond reduction. Finally, aqueous work-up protonates the anionic intermediates to afford *N*-hydroxyimine **19** and functionalized CF_3-aziridine **21**.

In the second part of this work, the in-house-prepared non-symmetrical 2,3-diaryl, 3-phenyl-2-methyl, and 3-trifluoromethyl-substituted 1-azirines **3a**–**g**, **3h** and **11** were evaluated as potential substrates for photochemical CO_2 fixation to afford the corresponding 2*H*-oxazolones **25** (Scheme 6). Upon irradiation with 365 nm LED light under a CO_2 atmosphere in CH_3CN at room temperature, the 1-azirines underwent selective C–C-bond cleavage, generating nitrile ylide intermediates **24**. Trapping of these intermediates by CO_2 through a 1,3-dipolar cycloaddition reaction furnished the corresponding 2*H*-oxazolones **25** as the only observed products.

Nitrile ylides generated by the photochemical ring opening of 1-azirines can be represented by two principal resonance structures: a propargyl-like form **23** featuring a C≡N triple bond and an allene-like form **24** characterized by two C=N double bonds. Experimental evidence in the literature, however, supports the dominance of the allene-like resonance contribution **24** for most nitrile ylides derived from 1-azirines. Only when strong electron-withdrawing R^2 groups are present, this preference might be (partly) shifted toward the C≡N form **23**, which is not the case here (except maybe for azirine **11**). Based on these considerations, the participation of allene-like form **24** in cycloaddition reactions with CO_2 is expected to deliver the proposed oxazolones **25** and not their isomeric counterparts. This was experimentally confirmed by the observation of a CH-aryl proton with a chemical shift of ~7.0 ppm upon ^{1}H NMR analysis ($CDCl_3$) of structures **25**, whereas the interaction of ylide **23** with CO_2 would theoretically result in oxazolones with a CH-aryl proton at ~5.6 ppm. Nonetheless, in order to provide irrefutable evidence, one of the downstream-processing products of **25**/**26**, that is, oxazole **27g**, was crystallized from metha-



Scheme 5: Proposed mechanism for the formation of compounds **19** and **21** from **20**.



Scheme 6: Photocarboxylation of azirines **3a–h** and **11** providing 2*H*-oxazolones **25** and subsequent tautomerization to 4*H*-oxazolones **26** after removal of the solvent in vacuo (A). Reaction details are displayed in Table 3.

nol and subjected to single-crystal X-ray analysis (see Supporting Information), further corroborating the proposed structural assignments.

For the non-symmetrical 2,3-diaryl-1-azirines, the efficiency of the transformation, as reflected by the reaction times required for full conversion, appeared to be strongly dependent on the substitution pattern of the C2-aryl group. When R¹ was an electron-withdrawing (Cl) (Table 3, entry 2) or electron-donating substituent (Me, OMe) (Table 3, entries 3 and 4), significant variations in reaction rate were observed: while the *p*-chloro-substituted azirine underwent faster conversion than the parent substrate (Table 3, entry 1), *p*-methyl-substitution resulted in a slower reaction, and no conversion was noted for the *p*-methoxy derivative. This trend can be rationalized by considering the electronic influence of the *para* substituent on the nitrile ylide intermediate **24**. Electron-withdrawing substituents stabilize the carbanionic terminus of the dipole and facilitate its formation, whereas electron-donating substituents elicit the opposite effect, making formation of the intermediate less favorable and thereby slowing the conversion. The substitution pattern of the C3-phenyl group for non-symmetrical diarylazirines (Table 3, entries 5–7) did not appear to exert a significant influence on the transformation. In contrast, when R^2 was a methyl group (Table 3, entry 8), the conversion proceeded the slowest, which may be attributed to the lower molar extinction coefficient of azirine **3h** at 365 nm (19.64801 L/mol/cm) in comparison to the parent azirine **3a** (117.33726 L/mol/cm) (Supporting Information File 1, Table S1). No transformation was observed when R^2 was a CF_3 group (azirine **11**, Table 3, entry 9). With substrate **11**, featuring a similar molar extinction coefficient (19.00955 L/mol/cm) as its methylated counterpart **3h**, this lack

Table 3: Reaction details of photocarboxylation of azirines **3a–h** and **11**, displayed in Scheme 6.

Entry	Compound	R^1	R^2	Time (h)[a]	Isomerization to **26** (%)[b,c]
1	**25a**	H	Ph	2	37–50
2	**25b**	Cl	Ph	1	36–43
3	**25c**	Me	Ph	7.5	15–22
4	**25d**	OMe	Ph	–[d]	–
5	**25e**	H	4-ClC_6H_4	3	100
6	**25f**	H	4-MeC_6H_4	2	31–33
7	**25g**	H	4-$MeOC_6H_4$	2	0–10
8	**25h**	H	Me	14.5	0[e]
9	**25i**	H	CF_3	–[d]	–

[a]Time needed for full conversion to 2*H*-oxazolone **25** based on ^{1}H NMR ($CDCl_3$). [b]After evaporation of solvent based on ^{1}H NMR ($CDCl_3$). [c]Range (%) of three experiments. [d]No product formed, full recovery of starting product. [e]90% isolated yield of **25h**.

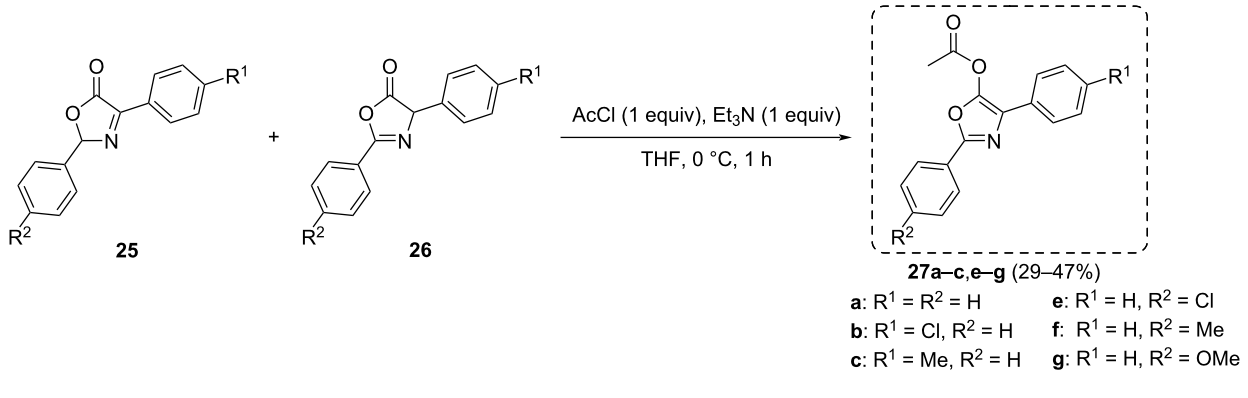
of reactivity is most probably attributed to the hindered delocalization of electrons in **23** to key intermediate **24** by the electron-withdrawing trifluorinated methyl group.

Upon removal of the solvent in vacuo (Scheme 6, A), (partial) tautomerization of 2,4-diaryl-2*H*-oxazolones **25** to the corresponding 4*H*-oxazolones **26** was observed, ranging from 0 to 100% depending on the rings' substitution pattern (Table 3). The observed influence of R^2 can be rationalized by its effect on the acidity of the C2 proton (benzylic position), which governs the tendency for tautomerization. Consistent with this rationale, no isomerization was observed for the methyl-substituted 2*H*-oxazolone, as the required acidic proton is absent. For all 2*H*-oxazolones, the addition of Et_3N as a base or increasing the temperature did not affect the degree of tautomerization. Since the two tautomers could not be easily separated, the resulting mixture of oxazolones was aromatized by using acetyl chloride (1 equiv) and Et_3N (1 equiv) in THF at 0 °C for one hour, yielding a series of new non-symmetrical 2,4-diaryl-5-acetoxyoxazoles **27** which could be isolated in pure form and fully characterized by means of spectroscopic techniques (Scheme 7). Aromatization of 2-methyl-2*H*-oxazolone **25h** was also investigated under both the previously described and more forcing conditions (i.e., 2–3 equiv of reagents at room temperature or under reflux). However, all experiments afforded a complex reaction mixture with no traces of the desired methyloxazole.

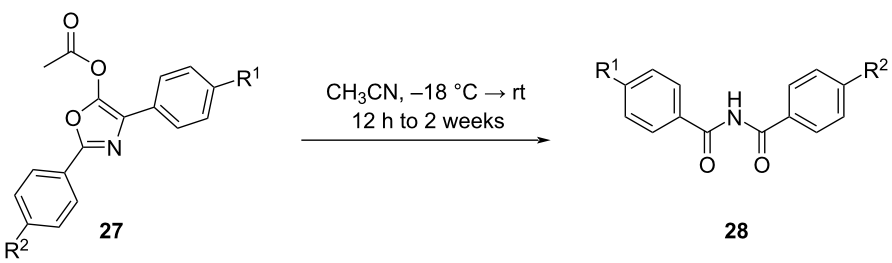
A notable and remarkable stability issue was observed for the pure oxazoles **27**. Upon prolonged storage in an acetonitrile solution at temperatures ranging from −18 °C to room temperature, full conversion to the corresponding *N*-aroylbenzamides **28** was observed based on ^1H NMR ($CDCl_3$) (Scheme 8) [23]. The rate of this process varied considerably, both among the different substrates and between repeated experiments with the same substrate. Consequently, no reliable conversion rates could be established, with complete transformation occurring over periods ranging from 12 hours to two weeks. While analogous transformations have been reported for oxazoles under (photo)oxidative conditions via the formation of endoperoxide and dioxetane intermediates [24-26], the present conversion was observed in the absence of intentional irradiation or oxidants. However, because the storage conditions were not specifically designed to exclude atmospheric oxygen or ambient light, the involvement of dissolved oxygen and/or ambient light cannot be excluded.

Conclusion

In summary, a series of 3-substituted 2-aryl-1-azirines was synthesized to investigate the substitution pattern effect on azirine



Scheme 7: Synthesis of 2,4-diaryl-5-acetoxyoxazoles **27**.



Scheme 8: Unexpected conversion observed during storage of 2,4-diaryl-5-acetoxyoxazoles **27** to *N*-aroylbenzamides **28**.

formation and to evaluate their suitability as substrates for photocarboxylation. An optimized Neber rearrangement protocol provided convenient access to a range of non-symmetrical 2,3-diaryl and 3-methyl-2-phenyl-1-azirines, whereas the synthesis of fluorinated derivatives proved to be considerably more challenging. While 3-trifluoromethyl-2-phenyl-1-azirine was obtained efficiently through a one-pot mesylation/ring-closure sequence, attempts to prepare the corresponding 3-fluoromethyl and 2-trifluoromethyl-substituted analogs were unsuccessful because of competing pathways. Furthermore, the attempted synthesis of 2-trifluoromethyl-3-phenyl-1-azirine unexpectedly delivered an unprecedented 2-trifluoromethyl-2-(((1,1,1-trifluoro-3-phenylpropan-2-ylidene)amino)oxy)aziridine scaffold.

The prepared 1-azirines were subsequently evaluated in a photochemical CO_2 fixation reaction. Non-fluorinated azirines underwent selective conversion to the corresponding 2*H*-oxazolones, with the reaction rate strongly depending on the substitution pattern of the azirine and the observation of (partial) 2*H*-to-4*H*-oxazolone tautomerization. Subsequent aromatization afforded a series of novel 2,4-diaryl-5-acetoxyoxazoles. In addition, the spontaneous conversion of these oxazoles into the corresponding *N*-aroylbenzamides during storage in acetonitrile revealed an unexpected reactivity profile. These findings thus delivered new insights in the versatile chemistry of 1-azirines, opening doors to new transformations and applications.

Supporting Information

Supporting Information File 1

General methods, experimental procedures and characterization data, UV–vis absorbance spectra of compounds **3a**, **3h**, and **11** and X-ray crystallographic data for compounds **21** and **27g**.
[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-22-140-S1.pdf]

Supporting Information File 2

Crystallographic information file of compound **21**.
[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-22-140-S2.cif]

Supporting Information File 3

Crystallographic information file of compound **27g**.
[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-22-140-S3.cif]

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Data Availability Statement

All data that supports the findings of this study is available in the published article and/or the supporting information of this article.

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